



Quality Improvement of Low Alcohol Craft Beer Produced by Evaporative Pertraction

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The non-alcoholic beverage industry is influenced by the trend of the consumers towards healthier diets and added convenience and greater health benefits in their beverage choices. With the world's changing approach to alcohol, operators need to find new beverages respect to the alcoholic ones. An alternative consists in the development of beverages similar to those alcoholic, but free of the negative effects of alcohol. Among various techniques for alcohol removal, evaporative pertraction is a simple and inexpensive process due to operating parameters and to the stripping agent (generally water) used. We previously applied this technique to the dealcoholization of a lager beer, but a depletion of volatile compounds was observed. In this work we aim at producing a craft beer with reduced alcohol content (less than 1.2%vol) and with good quality. In order to limit aroma compound loss, evaporative pertraction using carbonated hydroalcoholic solutions as stripping agents, instead of water, was used. Moreover, maltodextrins were added in the beverage at the end of the dealcoholization process, in order to increase body and mouthfeel of the beer. The influence of these parameters was evaluated in terms of ethanol removal and beer quality properties (turbidity, foam, colour, bitterness, polyphenols, antioxidant activity, aroma) for the production of low alcohol craft beer, that is worth drinking.

1. Introduction

The development of beverages that can influence consumers into more positive patterns of alcohol consumption is a very exciting challenge. The possibility of the improvement of public health without spoiling consumers' enjoyment or relaxation is an important objective that producers and off trade have grasped with enthusiasm. The lowering of alcohol content in normal beers, wines and alcoholic beverages contributes to reduce the alcohol amount consumed by customers, hopefully without them noticing any variance in quality or flavor. It is a hard challenge from a technological point of view to preserve the taste profile of the corresponding alcoholic product and to remove alcohol. Hence, in order to offer a wide range, availability and good taste profile of lower and non-alcoholic beverages with respect to the alcoholic ones (beers, wine, etc.), different studies were performed (Liguori et al., 2013a; Diban et al., 2013; Liguori et al., 2013b) and researches are continuously in progress. The aim of this work is to improve the quality of a craft beer undergone to alcohol removal by evaporative pertraction. In a preliminary study (Russo et al., 2013a), we evaluated the feasibility of utilizing permeate solutions of a previous process as stripping agents for alcohol removal from a lager beer. We found that some quality parameters (colour, pH, polyphenols and antioxidant activity) of beer did not change and a reduction of water consumption and minor environmental impact of the process were obtained. With respect to aroma compounds, we found (Liguori et al., 2015) a depletion of main volatile substances (higher alcohols, esters, aldehydes) of the same extent of beer dealcoholized by other physical techniques. Therefore, in this work, the dealcoholization of a craft beer was carried out using hydroalcoholic solutions, similar to the beer in terms of volatile compounds but at lower concentrations, to

reduce the concentration difference of these compounds between both sides of membrane and to limit their transfer. During the process, an increase in turbidity and a loss of foam formation and stability in beer was previously observed because of both oxygenation and reduction in CO₂ content. To reduce these disadvantages of the process that reflect changes in beer quality, the stripping solutions were saturated with carbon dioxide. Moreover, maltodextrins were added in low alcohol beer in order to increase body and mouthfeel of the beer. In fact, the mouthfeel of the beer comprises three key attributes, which are carbonation, palate fullness and aftertaste. The physical properties associated with the palate fullness are density and viscosity (Langstaff and Lewis, 1993). Maltodextrins are non-fermentable carbohydrates that enhance density and viscosity of beer and as consequence the body and palate fullness.

The quality of low alcohol craft beer was evaluated in comparison to the original one in terms of chemical and physical properties, such as: original extract, final extract, pH, colour, bitterness, turbidity, viscosity, total nitrogen, O₂ and CO₂ content, foam stability, polyphenols, antioxidant activity, volatile compounds.

2. Materials & methods

2.1 Materials

The beer (4.3 %vol) was produced at the 110 L pilot plant of CERB (Italian Brewing Research Centre, Perugia, Italy). The raw materials used for recipe formulation were the following: Monaco and Abbey malt from Weyermann® (Bamberg, Germany), Special B from Castle Malting® (Beloeil, Belgium). Hallertau Magnum from Barth Haas® (Nürnberg, Germany) was used for bittering the beer. S-04 from Fermentis® was added to ferment the wort (Marcq-en-Baroeul, France). The fermentation temperature was set at 20 °C. All reagents used for chemical analyses were analytical grade by Sigma Aldrich.

2.2 Lab scale plant and dealcoholization protocol

The lab scale plant was equipped with a membrane module, pumps, flowmeters, a manometer to check feed pressure at the inlet of module, a cooler to regulate the fluids temperature at 10°C and K-thermocouples to check fluids temperature. The membrane module (1x5.5 Liqui-Cel) has the following characteristics: polypropylene membrane, 1800 cm² surface area, 42 µm thickness and 14 cm length, 40% porosity, 0.03 µm membrane pore diameter. It consists of 2300 fibers with dimensions: 11.5 cm length, 220 µm inner diameter and 300 µm outer diameter. The feed (beer) and stripping streams (hydroalcoholic solutions) flowed inside the fibres and outside (shell side), respectively, at 70 and 140 mL/min. The reduction of alcohol content in beer was obtained dividing the process in cycles in order to modulate the initial composition of stripping solutions with respect to that of the beer. In fact, the dealcoholization kinetics studied in a previous work (Russo et al., 2013a) let to determine process time and alcohol content of stripping solutions to reach an alcohol concentration in beer less than 1.2 %vol. In this work, we used as stripping solutions hydroalcoholic solutions obtained by diluting the same beer undergone to the dealcoholization and then adding carbon dioxide up to saturation at ambient pressure.

For the dealcoholization of this craft beer, five cycles were necessary; each of them was performed with a new carbonated hydroalcoholic solution. The stripping solutions used were at decreasing ethanol concentrations with increasing the number of cycle (i.e. 0.8, 0.4, 0.2 %vol. respectively for 1st, 2nd and 3rd cycle and 0.1%vol for the last two cycles). The overall process time was 270 min: 75 and 60 min for the 1st and 2nd cycles respectively, and 45 min for the following three cycles. 15 g/L of commercial maltodextrins were added to the beer after the dealcoholization (A.C.E.F.).

2.3 Analyses

Chemical and physical analyses were carried out on the original and low alcohol beer. The alcohol content was measured by pycnometer. Other quality parameters, such as pH, colour, turbidity, original extract, final extract, total nitrogen, viscosity and bitterness were performed in accordance with Analytica EBC (Analytica EBC, 2010). The polyphenols content was determined by Folin-Ciocalteu assay (Singleton and Rossi, 1965). DPPH radical scavenging activity of beer was determined according to the method of Brand-Williams et al. (1995) with minor changes. The absorbance at 515 nm was measured after the solution had been allowed to stand in the dark for 40 min. A blank experiment was also carried out. The antioxidant activity was expressed as percentage inhibition of DPPH /µl of beer.

The volatile compounds in beer were determined according to Poiana et al. (2006) and Liguori et al. (2014) by a Gas Chromatograph 6850 (Agilent Technologies) equipped with a Mass Spectrometer 5975C coupled with

Maestro Autosamples Gerstel Multi-Purpose Sampler. Data analysis was performed using the MSD Chemstation Data Analysis Software (Agilent).

2.4 Statistical Analysis

Dealcoholization trials and analytical measurements were carried out in triplicate and mean values and standard deviation values were reported. Monofactorial variance analysis was used to determine significant differences ($p < 0.05$) between original and low alcohol craft beer by Analysis Lab software.

3. Results and discussion

The alcohol content in beer was investigated through the dealcoholization process (Figure 1). At each cycle, a reduction of ethanol in beer was observed while the stripping solutions gradually enriched in ethanol. The last two cycles are critical for the alcohol removal due to small differences between both sides of membrane. The final alcohol content of the beer was 0.7 %vol.

Several important quality parameters were checked in the original and low alcohol beer. Looking at the extract, the decrease in ethanol caused a variation of original, apparent and real extract (Table 1). In particular the original extract was lower than 8 degree Plato after the dealcoholization, thus in accordance with the Italian low-alcohol beer regulation (Reg. 1354/1962). No variation of pH was observed at the end of the process according to previous studies (Russo et al., 2013a,b; De Francesco et al., 2014). The colour of beer was very high both before and after the process and the values are not statistically different. The colour level is similar to dark beer style, e.g. Stout and Porter (BJCP, 2008). The bitterness is another important quality parameter of beer, which gives more equilibrium and balance to the beer. The bitter substances at the end of the process were similar to those in the original beer (Table 1). Similarly, total nitrogen and free amino nitrogen did not change significantly being non-volatile compounds; these results are in accordance with those reported in a previous study (De Francesco et al., 2014). Turbidity value differs in low alcohol beer with respect to the original one: a decrease occurred after the dealcoholization process, as reported in Table 1. This change may be due to the properties of the craft beer, which is an unfiltered beer. As expected, the viscosity of beer remained unaltered, most likely due to adjunct of the maltodextrins. A significant loss of carbon dioxide occurred in beer both due to the transfer through the membrane and to the stirring of streams during the process that facilitates this loss. Nonetheless, the final content of 2.9 g/L (Table 1) was due to both saturation of stripping solutions, which limits this loss in beverage, and carbonation at atmospheric pressure of low alcohol beer performed before bottling. The oxygen uptake was very low: its final content was equals 57 µg/L in low alcohol beer, a value usually found in bottled beer (O'Rourke, 2002).

While indiscriminate drinking of alcohol is undesirable, a positive dimension to the moderate consumption of beer may exist given that beer contains some health-promoting substances such as polyphenols and other molecules, responsible of antioxidant activity. In fact, as reported in Qi Yeo and Liu (2014), recent findings highlighted the interesting biological activities of hop prenylflavonoids, hence, the production of beer enriched with these substances is of huge interest to the brewing industry for their potential health benefits.

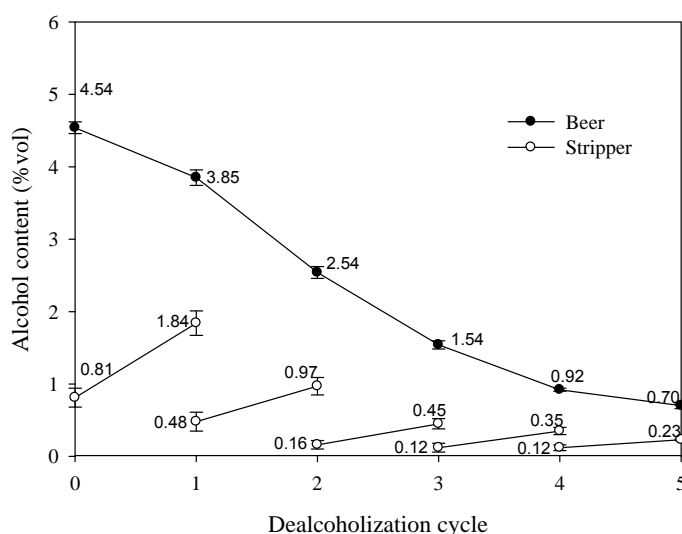


Figure 1: Alcohol content in beer and stripping solutions during dealcoholization process.

Table 1: Quality parameters content before and after the dealcoholization.

	Original Beer	Low alcohol Beer
Original Extract	12.1 ^a ± 0.1	7.8 ^b ± 0.1
Apparent Extract	4.2 ^b ± 0.06	6.67 ^a ± 0.08
Real Extract	5.7 ^b ± 0.1	6.8 ^a ± 0.1
Ethanol (%vol)	4.3 ^a ± 0.1	0.7 ^b ± 0.1
pH a 20°C (pH)	4.0 ^a ± 0.08	4.1 ^a ± 0.08
Colour (U-EBC)	107.5 ^a ± 6.0	119.4 ^a ± 6.7
Bitterness (BU)	20.0 ^a ± 3	17.0 ^a ± 2
Total Nitrogen (g L ⁻¹)	592.0 ^a ± 28	599.0 ^a ± 28
Free Amino Nitrogen (mg L ⁻¹)	43.0 ^a ± 8	49.0 ^a ± 9
Turbidity (U-EBC)	64.6 ^a ± 0.2	54.8 ^b ± 0.2
Viscosity (MPa s)	1.7 ^a ± 0.04	1.6 ^a ± 0.04
Carbon Dioxide (g L ⁻¹)	7.4 ^a ± 0.1	2.9 ^b ± 0.1
Oxygen (µg L ⁻¹)	8 ^a ± 2	57 ^b ± 2
Foam stability (s)	220 ± 5	ND
Polyphenols (mg GAE L ⁻¹)	781.0 ^a ± 9.5	829.1 ^b ± 26.5
Antioxidant activity (% / µL beer)	1.1 ^a ± 0.1	1.07 ^a ± 0.1

ND: not detectable. Values on the same row with different superscript letters are statistically different (p<0.05).

In this work, we evaluated the polyphenols content and the overall antioxidant activity in beer. Polyphenols have been considered the main natural antioxidants in brewing raw materials and beer, which contains a complex mixture of phenolic compounds extracted from malt and hops with antioxidant properties as described by Shahidi and Naczki (1995). Besides, polyphenols play a role in haze formation and flavor stability in beer (Aron and Shellhammer, 2010). As reported in Table 1, the concentration of polyphenols was about 800 mg GAE/L and a small change was found after the dealcoholization process. In beers, the phenolics amount varies in a wide range. In fact, in thirty-four beer samples investigated, Zhao et al. (2010) found a concentration ranging from 152.01 mg GAE/L for Reeb beer to 339.12 mg GAE/L for Carlsberg beer. Also as regards antioxidant activity, the beer exhibited strong DPPH radical scavenging activity and the values of the original and low alcohol beer were not significant different (p<0.05) (Table 1) and higher than those reported in literature (Harmanescu et al., 2006) (0.0026-0.3498 %/µL), as a result of the high polyphenols content.

Volatile compounds

The volatile profile is one of the main characteristics that determine the overall sensory and organoleptic properties of beer. Several volatile compounds, belonging to heterogeneous groups, such as, esters, alcohols, acids, aldehydes, ketones, sulphur compounds, etc., have been identified in beer. In many cases, these substances may influence the beer aroma and flavour by a synergistic or antagonistic effect. Thus, some volatiles contribute greatly to the beer flavour, while others are important merely in building up the background flavour of the product. Herein, the group of higher alcohols, esters, aldehydes and diketones were measured before and after the evaporative pertraction process. The driving force for mass transfer across the membrane is the concentration gradient resulting in vapour pressure differential. The migration is due to evaporation that occurs at ambient temperature and pressure, which is the main advantage of this membrane technology. It was unavoidable to stop this phenomenon due to the aroma compounds volatility, which causes the migration through the pores of the membrane, and the condensation into the stripping solutions. We tried to hinder this phenomenon by means of stripping solutions composition. To this aim, all the stripping solutions were obtained by diluting the beer undergone to the dealcoholization and then adding carbon dioxide up to saturation at ambient pressure.

With regard to higher alcohols, their loss percentage was very similar to the ethanol (Table 2), demonstrating a similar vapour pressure. Only 2-phenylethanol loss percentage was lower than ethanol and higher alcohols. Concerning the esters, the loss percentage was even higher than the ethanol due to higher volatility, as reported by previous studies (Russo et al., 2013a; De Francesco et al., 2014). In particular, ethyl acetate, the most abundant ester found in beer, and isoamyl acetate, one of the most important esters, which impart a distinctive banana flavour to beer, decreased considerably after the dealcoholization up to values lower than the taste threshold (Table 2). Aldehydes are usually recognized off-flavour of beer and their content increased during storage or by oxidation (Hashimoto, 1972). An increase of acetaldehyde, 2-methylbutanal, 3-methylbutanal and hexanal occurred. This behaviour may be due to different causes, such as oxidation of alcohols, low volatility, less water solubility than other volatile compounds. On the contrary, furfuraldehyde, 3-methylpropionaldehyde and 2-phenylacetaldehyde, aging key components, decreased after the dealcoholization (Table 2). Anyway, the amount of each aldehyde found in low alcohol beer was below the taste threshold (Meilgaard, 1975).

Table 2: Volatile compounds content before and after the dealcoholization.

Volatile compounds	Original Beer	Low alcohol Beer	Loss Percentage (%)
<i>Higher alcohols</i>			
n-Propanol (mg L ⁻¹)	14.4 ^a ± 0.1	2.7 ^b ± 0.1	81.3
Isobutanol (mg L ⁻¹)	41.4 ^a ± 0.9	7.0 ^b ± 0.2	83.1
3-methylbutanol (mg L ⁻¹)	43.2 ^a ± 1.1	8.8 ^b ± 0.4	79.6
2-methylbutanol (mg L ⁻¹)	17.3 ^a ± 0.4	3.1 ^b ± 0.1	82.1
Furfuryl alcohol (mg L ⁻¹)	2.7 ^a ± 0.1	1.0 ^b ± 0.1	63.0
2-Phenylethanol (mg L ⁻¹)	23.6 ^a ± 0.4	14.5 ^b ± 0.1	38.6
Σ higher alcohols (mg L⁻¹)	142.6^a ± 3	37.1^b ± 1	74.0
<i>Esters</i>			
Ethyl acetate (mg L ⁻¹)	6.3 ^a ± 0.2	0.5 ^b ± 0.01	92.1
Ethyl butanoate (mg L ⁻¹)	ND	ND	-
Isoamyl acetate (mg L ⁻¹)	0.2 ^a ± 0.01	0.03 ^b ± 0.01	85.0
Ethyl hexanoate (mg L ⁻¹)	0.02 ^a ± 0.01	0.02 ^a ± 0.01	0.0
Ethyl octanoate (mg L ⁻¹)	0.03 ^a ± 0.01	0.02 ^a ± 0.01	33.3
Σ ester (mg L⁻¹)	6.55^a ± 0.23	0.57^b ± 0.04	91.3
<i>Aldehydes</i>			
Acetaldehyde (µg L ⁻¹)	10784.8 ^a ± 1215.2	17873.1 ^b ± 831.6	- 65.7
2-Methylbutanal (µg L ⁻¹)	50.2 ^a ± 4.6	50.6 ^a ± 5.4	- 0.8
3-Methylbutanal (µg L ⁻¹)	106.1 ^a ± 8.4	106.9 ^a ± 15.4	- 0.8
Hexanal (µg L ⁻¹)	3.3 ^b ± 0.3	8.2 ^a ± 0.4	-148.5
Furfuraldehyde (µg L ⁻¹)	373.6 ^a ± 12.9	37.5 ^b ± 1.9	90.0
3-Methylpropionaldehyde (µg L ⁻¹)	49.9 ^a ± 2.7	19.8 ^b ± 1.7	60.3
2-Phenylacetaldehyde (µg L ⁻¹)	51.2 ^a ± 4.4	49.3 ^a ± 0.4	3.7
Σ aldehydes (µg L⁻¹)	11419.1^a ± 1248.5	18145.4^b ± 856.8	- 58.9
<i>Ketons</i>			
Diacetyl (µg L ⁻¹)	76.2 ^a ± 4.2	58.5 ^b ± 8.4	23.2
2,3 pentanedione (µg L ⁻¹)	28.2 ^a ± 1.6	20.9 ^b ± 3.1	25.9
Σ diketones (µg L⁻¹)	104.4^a ± 5.8	79.4^b ± 11.5	23.9

ND: not detectable. Values on the same row with different superscript letters are statistically different (p<0.05).

Diketones are another group of volatile compounds, which are responsible for the butter-like aroma of beer, especially diacetyl and 2,3-pentanedione. Their concentration was statistically different in original and low alcohol beers, remaining below taste threshold throughout the process (Table 2).

The overall effect of operating parameters applied for the dealcoholization of this craft beer allowed to obtain a lower loss of aldehydes and ketons than those reported by Russo et al. (2013b), where pure water as stripping agent was used for the dealcoholization of a lager beer. In fact the percentage loss of these volatile compounds in lager beer were 97 and 99%, respectively. Only for higher alcohols the depletion was higher than in lager beer (62%), while no significant difference (p<0.05) in esters loss was found. A further study on dealcoholization of lager beer was performed using permeates of a previous dealcoholization process as stripping agents (Liguori et al., 2015). The loss of volatile compounds classes observed was respectively of 77% for higher alcohols, 99% for esters and 93% for aldehydes.

4. Conclusions

This study was focused on the production of low alcohol craft beer by means of evaporative pertraction. The low alcohol beer at 0.7 %vol was obtained by using carbonated hydroalcoholic solutions as stripping agents and adding maltodextrins at the end of the dealcoholization process. These efforts allowed to hinder loss of volatile compounds. In fact, the loss of volatile compounds was observed respectively of 74% for higher alcohols, 91% for esters, 59% for aldehydes and 24% for ketons; the loss of aldehydes and ketons are lower than previous results on beer dealcoholization by this technique. Results of conventional beer parameters such as colour, bitterness, viscosity, polyphenols, antioxidant activity showed no significant differences between original and low alcohol beer. Oxygenation phenomenon was limited by carbonation both of stripping solutions and of low alcohol beer before bottling. Future work will investigate the sensory evaluation of low alcohol craft beer to test the effect of maltodextrins adjunct in beer after dealcoholization process. Improvement of sensory quality should allow to increase consumer's acceptance of low alcohol beers and cover the light-products market segments in a more extended way.

References

- Analytica-EBC. Verlag Hans Carl: Nurnberg: 2010.
- Aron P. M., Shellhammer T.H., 2010, A Discussion of Polyphenols in Beer Physical and Flavour Stability, *J. Inst. Brew.* 116, 4, 369–380.
- BJCP, 2008, Beer Judge Certification Program Style Guidelines for Beer, Mead and Cider, 2008, BJCP, Inc.
- Brand-Williams W., Cuvelier M. E., Berset C., 1995, Use of a free radical method to evaluate antioxidant activity. *Leben. Wiss. Und Techn.* 28, 25-30.
- De Francesco G., Freeman G., Lee E., Marconi O., Perretti G., 2014, Effect of operating conditions during low-alcohol beer production by osmotic distillation, *J Agri.Food Chem.* 62 (14), 3279–3286.
- Diban N, Arruti A., Barceló A., Puxeu, M., Urtiaga A., Ortiz I., 2013, Membrane dealcoholization of different wine varieties reducing aroma losses. Modeling and experimental validation, *Innov. Food Sci. Emerg.Technol.* 20, 259-268.
- Harmanescu M., Gergen I., Isengard H., 2006, Correlation between total antioxidant capacity and polyphenols content for some beer types. *J. Agroalim. Proc. Technol.* 12, 2, 371-376.
- Hashimoto N., 1972, Oxidation of higher alcohols by melanoidins in beer, *J Inst. Brew* 78, 1, 43–51.
- Langstaff S.A., Lewis M.J., 1993, The mouthfeel of beer - a review. *J Inst. Brew.* 99, 31–37
- Liguori L., Russo P., Albanese D., Di Matteo M., 2013a, Evolution of quality parameters during red wine dealcoholization by osmotic distillation. *Food Chem* 140, 68–75.
- Liguori L., Russo P., Albanese D., Di Matteo M., 2013b, Effect of Process Parameters on Partial Dealcoholization of Wine by Osmotic Distillation. *Food Bioprocess Technol* 6, 2514-2524.
- Liguori L., De Francesco G., Russo P., Perretti G., Albanese D., Di Matteo M., 2015, Production and characterization of alcohol-free beer by membrane process. *Food Bioprod Process*, DOI: 10.1016/j.fbp.2015.03.003.
- Meilgaard M.C., 1975, Flavor chemistry of beer: part ii: flavor and threshold of 239 aroma volatiles, *MBAA Technical Quarterly*, 12, 3, 151-168.
- O'Rourke T., 2002, Technical summary 3: the role of oxygen in brewing, *The Brewer International*, 45-47.
- Poiana M., Attanasio A., Albanese D., Di Matteo M., 2006, Alcoholic extracts composition from lemon fruits of the Amalfi-Sorrento peninsula. *J. Essent. Oil Res.* 18, 4, 432-437.
- Reg. n.1354 of 16 august 1962. Hygiene control of the production and trade of beer. *Gazz. Uff.* n.234 of 17 september, 1962
- Russo P., Liguori L., Albanese D., Crescitelli A., Di Matteo M., 2013a, Investigation of Osmotic Distillation Technique for Beer Dealcoholization. *Chem. Eng. Trans.* 32, 1735-1740.
- Russo P., Liguori L., Albanese D., Crescitelli A., De Francesco G., Perretti G., Di Matteo M., 2013b, Investigation of Osmotic Distillation Technique for Beer Dealcoholization, *AIDIC Conference Series*, 11, 311-320 DOI: 10.3303/ACOS1311032
- Shahidi F., Naczk M., 1995, Food Phenolics; Sources, Chemistry, Effects, Applications. Technomic Publishing Co. Inc., Lancaster: 10–13.
- Qi Yeo H, Liu S.Q., 2014, An overview of selected specialty beers: developments, challenges and prospects. *Int. J. Food Sci. Technol.*, DOI:10.1111/ijfs.12488.
- Singleton V., Rossi J. Jr., 1965, Colorimetry of total phenolics with phosphomolybdic phosphotungstic acid reagents. *Am. J. Enol. Viticult.* 16, 144–158.
- Zhao H., Chen W., Lu J., Zhao M., 2010, Phenolic profiles and antioxidant activities of commercial beers. *Food Chem.* 119, 1150–1158.